

Patentanwaltskanzlei
Luderschmidt, Schüler und Partner
Frau Susanne Krebs
John-F.-Kennedy-Straße 4

65189 Wiesbaden

TRANSLATOR'S VERIFICATION

We, LINGO Language Services GmbH, Westenhellweg 85-89, 44137 Dortmund/Germany, represented by Eric LINGO, managing director, hereby certify that the following translation that we have prepared, totalling 26 pages, is a true and correct translation from German into English of a document presented to us as a copy:

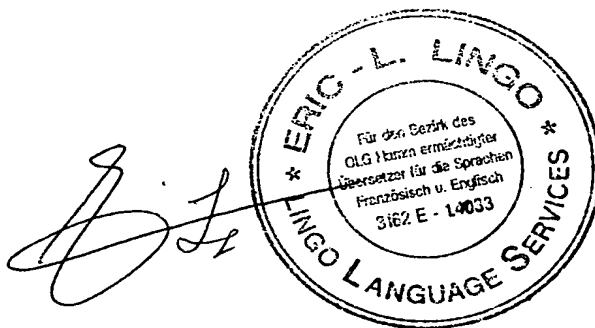
Patent specifications: International Patent Application No. PCT/EP 03 / 02399
(Claims / Description / Abstract)

Title: DE: Verfahren zur Herstellung einer Polymerelektrolytmembran
und deren Anwendung in Brennstoffzellen

EN: Method for producing a polymer electrolyte membrane and
application thereof in fuel cells

Applicant: Celanese Ventures GmbH
Frankfurt am Main/DE

Place, date: Dortmund, 21 July 2008



FEDERAL REPUBLIC OF GERMANY

Certification of priority for the filing of a patent application

File number: 102 09 419.5

Application date: 05 March 2002

Applicant/Owner: Celanese Ventures GmbH, Frankfurt Main/Germany

Title: Method for producing a polymer electrolyte
membrane and application thereof in fuel cells

IPC: B 01 D, H 01 M

**The attachments to this application are a true and accurate reproduction
of the original documents of this patent application.**

Munich, 05 June 2003

German Patent and Trade Mark Office

The President

p.p.

[signature illegible]

Weihmayr

Method for producing a polymer electrolyte membrane and application thereof in fuel cells

The present invention relates to a proton-conducting polymer electrolyte membrane based on polyvinylphosphonic acid polymers which can, owing to its excellent chemical and thermal properties, be used for a variety of purposes and is particularly suitable as a polymer electrolyte membrane (PEM) in so-called PEM fuel cells.

A fuel cell usually contains an electrolyte and two electrodes separated by the electrolyte. In the case of a fuel cell, one of the two electrodes is supplied with a fuel, such as hydrogen gas or a methanol-water mixture, and the other electrode is supplied with an oxidant, such as oxygen gas or air, and through this, chemical energy from the fuel oxidation is directly converted into electric energy. Protons and electrons are formed in the oxidation reaction.

The electrolyte is permeable to hydrogen ions, i.e. protons, but not for reactive fuels, such as the hydrogen gas or methanol and the oxygen gas.

Typically, a fuel cell comprises several individual cells, so-called MEUs (membrane electrode units), each of which contains an electrolyte and two electrodes separated by the electrolyte.

As electrolyte for the fuel cell, solids, such as polymer electrolyte membranes, or liquids, such as phosphoric acid, are applied. Polymer electrolyte membranes have recently attracted interest as electrolytes for fuel cells. In principle, it is possible to differentiate between 2 categories of polymer membranes.

The first category includes cation exchange membranes consisting of a polymer frame which contains covalently bonded acid groups, preferably sulphonic acid groups. The sulphonic acid group converts into an anion with donation of a hydrogen ion and therefore conducts protons. Here, the mobility of the proton and thus the proton conductivity is directly linked to the water content. Because of the very good

miscibility of methanol and water, such cation exchange membranes have a high permeability to methanol and are therefore unsuitable for applications in a direct methanol fuel cell. If the membrane dries out, i.e. as a result of a high temperature, the conductivity of the membrane and consequently the performance of the fuel cell decrease dramatically. The operating temperatures of fuel cells containing such cation exchange membranes are thus limited to the boiling temperature of water. Humidification of the fuels presents a major technical challenge to the use of polymer electrolyte membrane fuel cells (PEM-FC), in which conventional, sulphonated membranes such as, e.g., Nafion are used.

Thus, for example, perfluorosulphonic acid polymers are used as materials for polymer electrolyte membranes. The perfluorosulphonic acid polymer (such as, e.g., Nafion) generally has a perfluorohydrocarbon skeleton, such as a copolymer of tetrafluoroethylene and trifluorovinyl, and a side chain bonded to this with a sulphonic acid group, such as a side chain with a sulphonic acid group bonded to a perfluoroalkylene group.

The cation exchange membranes preferably are organic polymers with covalently bonded acid groups, in particular sulphonic acid. Methods for the sulphonation of polymers are described in F. Kucera et al., Polymer Engineering and Science 1988, Vol. 38, No. 5, 783-792.

In the following, the most important types of cation exchange membranes are listed which have achieved commercial significance in terms of the use in fuel cells.

The most important exponent is the perfluorosulphonic acid polymer Nafion® (US 3692569). As described in US 4453991, this polymer can be brought into solution and then used as ionomer. Cation exchange membranes are also obtained by filling a porous support material with such an ionomer. In this connection, expanded Teflon is preferred as the support material (US 5635041).

Another perfluorinated cation exchange membrane can be produced by copolymerisation of trifluorostyrene and sulphonyl-modified trifluorostyrene, as described in US5422411. Composite membranes consisting of a porous support material, in particular expanded Teflon, filled with ionomers consisting of such sulphonyl-modified trifluorostyrene copolymers are described in US5834523.

US6110616 describes copolymers of butadiene and styrene and their subsequent sulphonation for the production of cation exchange membranes for fuel cells.

Another class of partly fluorinated cation exchange membranes can be produced by laser grafting and subsequent sulphonation. Here, as described in EP667983 or DE19844645, a grafting reaction is carried out on a previously irradiated polymer film, preferably with styrene. In a subsequent sulphonation reaction, the sulphonation of the side chains then takes place. A cross-linking can also be performed simultaneously with the grafting and thus the mechanical properties can be changed.

Besides above membranes, another class of non-fluorinated polymers has been developed by sulphonation of thermoplastics stable at high temperatures. For example, membranes made of sulphonated polyether ketones (DE4219077, EP96/01177), sulphonated polysulphone (J. Membr. Sci. 83 (1993) p. 211) or sulphonated polyphenylene sulphide (DE19527435) are known.

Ionomers produced from sulphonated polyether ketones are described in WO 00/15691.

Furthermore, acid-base blend membranes are known which, as described in DE19817374 or WO 01/18894, are produced by mixtures of sulphonated polymers and alkaline polymers.

To further improve the membrane properties, a cation exchange membrane known from the prior art can be mixed with a polymer stable at high temperatures. The production and properties of cation exchange membranes consisting of blends of sulphonated PEK and a) polysulphones (DE4422158), b) aromatic polyamides (42445264) or c) polybenzimidazole (DE19851498) are described.

A disadvantage of all these cation exchange membranes is the fact that the membrane must be humidified, the operating temperature is limited to 100°C, and the membranes have a high permeability to methanol. The reason for these disadvantages is the conductivity mechanism of the membrane in which the transport of the protons is linked to the transport of the water molecule. This is referred to as "vehicle mechanism" (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

Polymer electrolyte membranes with complexes of alkaline polymers and strong acids have been developed as a second category. Thus, WO96/13872 and the corresponding US patent application 5,525,436 describe a method for the production of a proton-conducting polymer electrolyte membrane in which an alkaline polymer, such as polybenzimidazole, is treated with a strong acid, such as phosphoric acid, sulphuric acid etc.

The doping of a polybenzimidazole in phosphoric acid is described in *J. Electrochem. Soc.*, Volume 142, No. 7, 1995, p. L121-L123.

With the alkaline polymer membranes known in the prior art, the mineral acid employed (usually concentrated phosphoric acid) – to achieve the necessary proton conductivity - is either used after forming or alternatively, the alkaline polymer membrane is produced directly from polyphosphoric acid as in German patent applications No. 10117686.4, No. 10144815.5 and No. 10117687.2. In doing so, the polymer serves as a support for the electrolyte consisting of the highly concentrated phosphoric acid or polyphosphoric acid, respectively. In this connection, the polymer membrane fulfils further essential functions, in particular, it has to exhibit a high mechanical stability and serve as a separator for the two fuels mentioned at the outset.

An essential advantage of such a membrane doped with phosphoric acid or polyphosphoric acid is the fact that a fuel cell in which such a polymer electrolyte membrane is employed can be operated at temperatures above 100°C without the humidification of the fuels otherwise necessary. This is due to the characteristic of the phosphoric acid to be able to transport the protons without additional water via the so-called Grotthus mechanism (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

Further advantages for the fuel cell system are achieved through the possibility of operation at temperatures above 100°C. On the one hand, the sensitivity of the Pt catalyst to gas impurities, in particular CO, is reduced substantially. CO is formed as a by-product in the reforming of hydrogen-rich gas from carbon-containing compounds, such as, e.g., natural gas, methanol or benzene, or also as an intermediate product in the direct oxidation of methanol. Typically, the CO content of

the fuel has to be lower than 100 ppm at temperatures of $<100^{\circ}\text{C}$. However, at temperatures in the range of $150\text{--}200^{\circ}$, 10,000 ppm CO or more can also be tolerated (N. J. Bjerrum et. al., Journal of Applied Electrochemistry, 2001, 31, 773-779). This results in substantial simplifications of the upstream reforming process and therefore reductions of the cost of the entire fuel cell system.

A great advantage of fuel cells is the fact that, in the electrochemical reaction, the energy of the fuel is directly converted into electric energy and heat. In the process, water is formed at the cathode as a reaction product. Heat is also produced in the electrochemical reaction as a by-product. In applications in which only the power for the operation of electric motors is utilised, such as, e.g., in automotive applications, or as a versatile replacement of battery systems, the heat has to be dissipated to prevent overheating of the system. Additional energy-consuming devices which further reduce the total electric efficiency of the fuel cell are then needed for cooling. In stationary applications, such as for the centralised or decentralised generation of electricity and heat, the heat can be used efficiently by existing technologies, such as, e.g., heat exchangers. In doing so, high temperatures are aimed for to increase the efficiency. If the operating temperature is higher than 100°C and the temperature difference between the ambient temperature and the operating temperature is high, it will be possible to cool the fuel cell system more efficiently, for example using small cooling surfaces and dispensing with additional devices, in comparison to fuel cells which have to be operated at less than 100°C due to the humidification of the membrane.

Apart from these advantages, however, such a fuel cell system also has an essential disadvantage. Thus, phosphoric acid or polyphosphoric acid is present as an electrolyte which is not permanently bonded to the alkaline polymer by ionic interactions and can be washed out by water. As described above, water is formed at the cathode during the electrochemical reaction. If the operating temperature is above 100°C , the majority of the water is discharged as vapour via the gas diffusion electrode and the acid loss is very low. If the operating temperature drops below 100°C , however, e.g., when starting and shutting down the cell or in partial-load operation if a high power yield is aimed for, the water formed condenses and can

lead to more intense washing out of the electrolyte, highly concentrated phosphoric acid or polyphosphoric acid.

In the above-described method of operation of the fuel cell, this can lead to a constant loss of conductivity and cell performance which can lower the lifetime of the fuel cell.

A methanol-water mixture is used as the fuel for oxidation in the so-called direct methanol fuel cell (DMFC). During the required direct contact of the membrane doped with phosphoric acid or polyphosphoric acid with the aqueous fuel mixture at the anode, a constant washing out of the electrolyte and therefore an irreversible drop in performance results. Thus, polymer electrolyte membranes doped with phosphoric acid or polyphosphoric acid are not suitable for use in a direct methanol fuel cell.

Therefore, the present invention has the object to provide a novel polymer electrolyte membrane which avoids the washing out of the electrolyte. In particular, it should be possible to thus extend the operating temperature from $<0^{\circ}\text{C}$ up to 200°C and the system not requiring any humidification. A fuel cell containing a polymer electrolyte membrane according to the invention should be suitable for pure hydrogen and for numerous carbon-containing fuels, in particular natural gas, benzene, methanol and biomass.

This object is achieved through the production of a vinylphosphonic acid-containing solution and a method for producing a polymer electrolyte membrane by swelling a film made of a polymer stable at high temperatures in this solution and subsequently polymerising it to a polyvinylphosphonic acid polymer. Due to the high concentration of polyvinylphosphonic acid polymer, its high chain flexibility and the high acid strength of the polyvinylphosphonic acid, the conductivity is based on the Grotthus mechanism and the system therefore requires no additional humidification. The polymeric polyvinylphosphonic acid which can also be cross-linked by reactive groups forms an interpenetrating network with the polymer stable at high temperatures and is not washed out by product water formed or the aqueous fuel in the case of a DMFC. A polymer electrolyte membrane according to the invention has a very low permeability to methanol and is particularly suited for use in a DMFC.

Thus, an operation of a fuel cell over the long term is possible with a number of fuels such as hydrogen, natural gas, benzine, methanol or biomass.

Therefore, the object of the present invention is a proton-conducting electrolyte membrane which can be obtained by a method comprising the steps of

- A. swelling a film made of at least one polymer in a vinylphosphonic acid-containing solution and
- B. polymerising the present vinylphosphonic acid-containing solution introduced in step A).

The film made of at least one polymer used in step A) is a film that has a swelling of at least 3% in the vinylphosphonic acid-containing solution. Swelling is understood to mean an increase in weight of the film by at least 3% by weight. Preferably, the swelling is at least 5%, particularly preferably at least 10%.

The determination of swelling Q is determined gravimetrically from the mass of the film before swelling, m_0 and the mass of the film after polymerisation in accordance with step B), m_2 .

$$Q = (m_2 - m_0) / m_0 \times 100$$

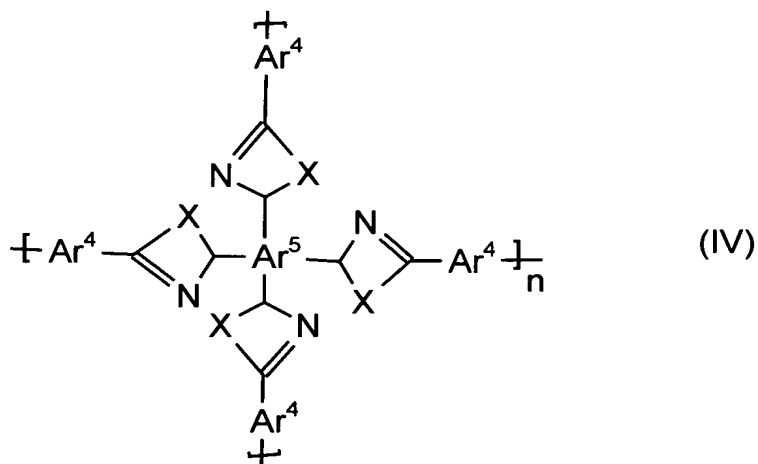
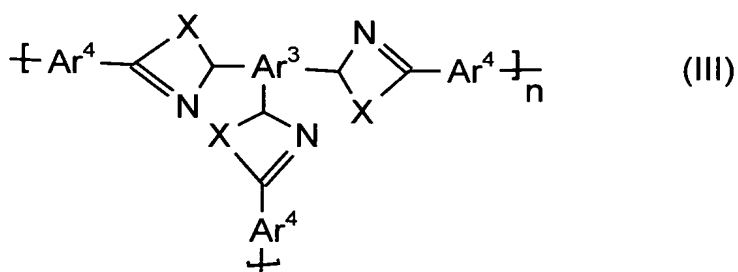
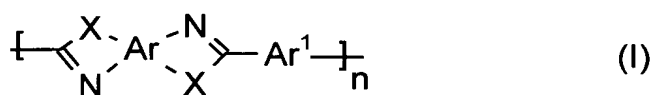
The swelling takes place at a temperature of more than 0°C, preferably between room temperature (20°C) and 180°C, in a vinylphosphonic acid-containing solution which contains at least 5% by weight of vinylphosphonic acid.

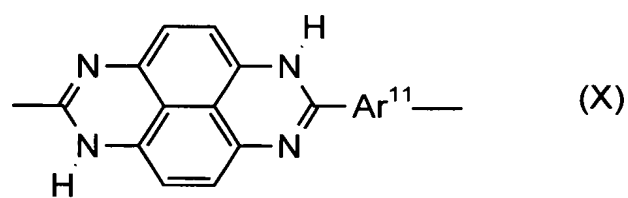
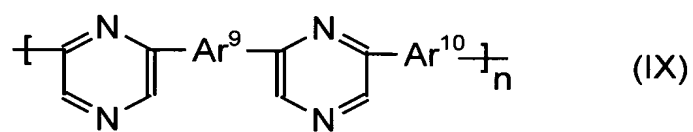
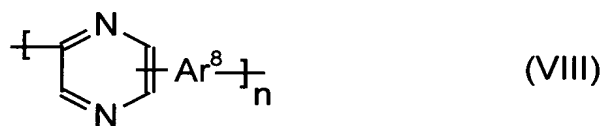
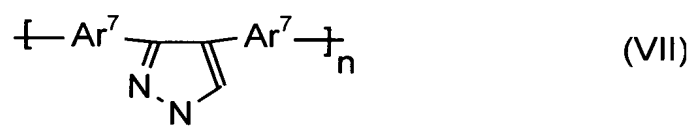
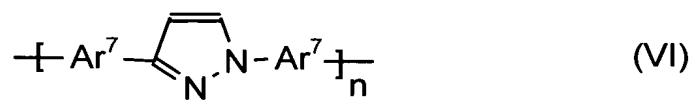
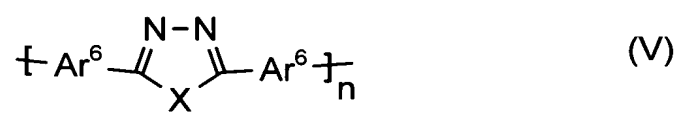
The polymers used in step A) are preferably polymers stable at high temperatures which contain at least one nitrogen, oxygen and/or sulphur atom in one or different repeating units.

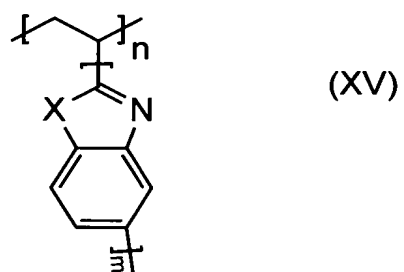
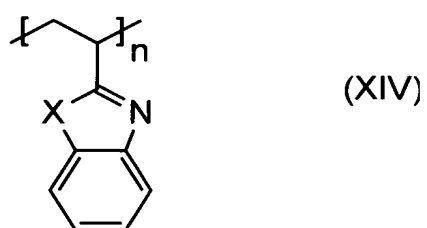
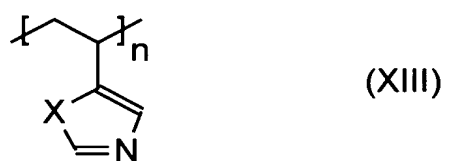
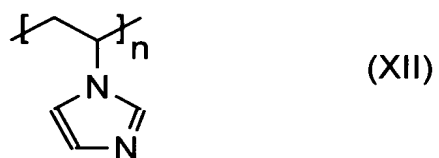
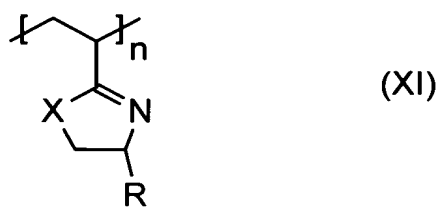
Particular preference is given to polymers which contain at least one nitrogen atom in a repeating unit. Special preference is given to polymers which contain at least one aromatic ring with at least one nitrogen heteroatom per repeating unit. From this group, polymers based on polyazoles are particularly preferred. These alkaline polyazole polymers contain at least one aromatic ring with at least one nitrogen heteroatom per repeating unit.

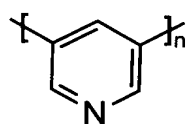
The aromatic ring is preferably a five-membered or six-membered ring with one to three nitrogen atoms, which may be fused to another ring, in particular another aromatic ring.

- 5 The alkaline polymer based on polyazole contains recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)

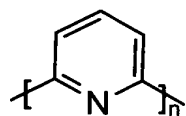




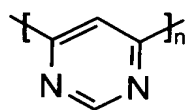




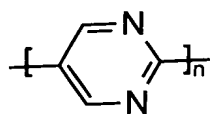
(XVI)



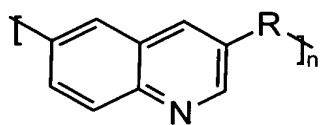
(XVII)



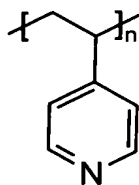
(XVIII)



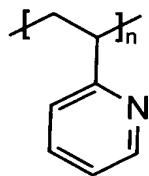
(XIX)



(XX)



(XXI)



(XXII)

wherein

Ar are the same or different and are each a tetravalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar¹ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar² are the same or different and are each a divalent or trivalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar³ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁴ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁵ are the same or different and are each a tetravalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁶ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁷ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁸ are the same or different and are each a trivalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar⁹ are the same or different and are each a divalent or trivalent or tetravalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar¹⁰ are the same or different and are each a divalent or trivalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

Ar¹¹ are the same or different and are each a divalent aromatic or heteroaromatic group which may be mononuclear or polynuclear,

X are identical or different and represent oxygen, sulphur or an amino group which carries a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as a further radical,

R are identical or different and represent hydrogen, an alkyl group and an aromatic group, and

n, m are each an integer greater than or equal to 10, preferably greater than or equal to 100.

Preferred aromatic or heteroaromatic groups are derived from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenylsulphone, quinoline, pyridine, bipyridine, pyridazine, pyrimidines, pyrazine, triazine, tetrazine, pyrrole, pyrazole, anthracene, benzopyrrole, benzotriazole, benzooxathiadiazole, benzooxadiazole, benzopyridine, benzopyrazine, benzopyrazidine, benzopyrimidine, benzopyrazine, benzotriazine, indolizine, quinolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, aziridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridizine, benzopteridine, phenanthroline and phenanthrene which optionally also can be substituted.

In this case, Ar¹, Ar⁴, Ar⁶, Ar⁷, Ar⁸, Ar⁹, Ar¹⁰, Ar¹¹ can have any substitution pattern, in the case of phenylene, for example, Ar¹, Ar⁴, Ar⁶, Ar⁷, Ar⁸, Ar⁹, Ar¹⁰, Ar¹¹ can be ortho-phenylene, meta-phenylene and para-phenylene. Particularly preferred groups are derived from benzene and biphenylene, which may also be substituted.

Preferred alkyl groups are short-chain alkyl groups having from 1 to 4 carbon atoms, such as, e.g., methyl, ethyl, n-propyl or isopropyl and t-butyl groups.

Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and the aromatic groups can be substituted.

Preferred substituents are halogen atoms, such as, e.g., fluorine, amino groups, hydroxy groups or short-chain alkyl groups, such as, e.g., methyl or ethyl groups.

Preference is given to polyazoles having recurring units of the formula (I) in which the radicals X within a recurring unit are identical.

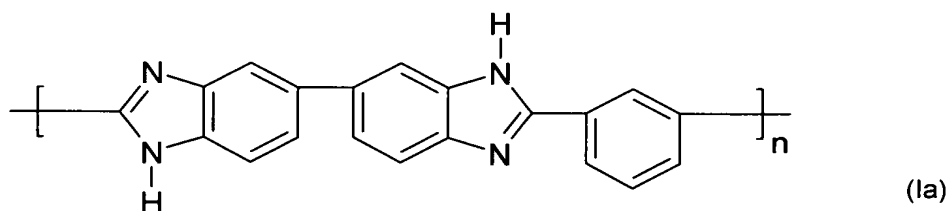
The polyazoles can in principle also have different recurring units wherein their radicals X are different, for example. However, there are preferably only identical radicals X in a recurring unit.

In another embodiment of the present invention, the polymer stable at high temperatures and containing recurring azole units is a copolymer or a blend which contains at least two units of the formula (I) and/or (II) which differ from one another.

In a particularly preferred embodiment of the present invention, the polymer containing recurring azole units is a polyazole, which only contains units of the formulae (I) and/or (II).

The number of recurring azole units in the polymer is preferably an integer greater than or equal to 10. Particularly preferred polymers contain at least 100 recurring azole units.

Within the scope of the present invention, preference is given to polymers containing recurring benzimidazole units. An example of an extremely practicable polymer containing recurring benzimidazole units is reflected by formula (Ia):



where n is an integer greater than or equal to 10, preferably greater than or equal to 100.

Further preferred polyazole polymers are polyimidazoles, polybenzothiazoles, polybenzoxazoles, polytriazoles, polyoxadiazoles, polythiadiazoles, polypyrazoles, polyquinoxalines, poly(pyridines), poly(pyrimidines) and poly(tetrazapyrenes).

Particular preference is given to Celazole from the company Celanese, in particular to one in which the polymer worked up by sieving as described in German patent application No. 10129458.1 is used.

In addition to the above-mentioned polymer, a blend which contains further polymers can also be employed. However, this polymer has to have the required stability at high temperatures. In this case, the function of the blend component is essentially to improve the mechanical properties and reduce the cost of material. Here,
5 polyethersulphone is a preferred blend component, as described in German patent application No. 10052242.4.

Additionally, the polymer film can feature further modifications, for example by cross-linking, as described in German patent application No. 1010752.8 or in WO
10 00/44816. In one preferred embodiment, the polymer film made of an alkaline polymer and at least one blend component and used for swelling additionally contains a crosslinker, as described in German patent application No. 10140147.7.

In addition, it is advantageous when the polymer film used for swelling is treated
15 beforehand, as described in German patent application No. 10109829.4. This variant is advantageous to increase the swelling of the polymer film.

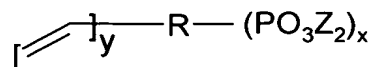
Instead of the polymer membranes produced by means of classical processes, it is also possible to use the polyazole-containing polymer membranes, as described in
20 German patent applications No. 10117686.4, 10144815.5, 10117687.2. To this end, these are freed from the polyphosphoric acid and/or phosphoric acid and used in step A).

Within the context of the present invention, stable at high temperatures means a
25 polymer which, as a polymeric electrolyte, can be operated over the long term in a fuel cell at temperatures above 120°C.

The polymer membrane according to the invention can contain even more additives in the form of fillers and/or auxiliary materials.

30 The polyazoles used, in particular, however, the polybenzimidazoles are characterized by a high molecular weight. Measured as the intrinsic viscosity, this is preferably at least 0.2 dl/g, preferably 0.8 to 10 dl/g, in particular 1 to 10 dl/g.

The solution of vinyl-containing phosphonic acids used in step A) is a compound of the formula



wherein

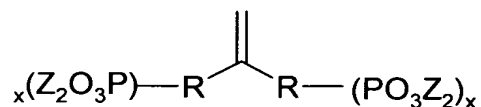
R is a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group, or a C5-C20 aryl or heteroaryl group, wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, COOZ, -CN, NZ₂,

Z represent, independently of another, hydrogen, a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group or a C5-C20 aryl or heteroaryl group wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, -CN, and

x represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

y represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or of the formula



wherein

R is a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group, or a C5-C20 aryl or heteroaryl group, wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, COOZ, -CN, NZ₂,

Z represent, independently of another, hydrogen, a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group or a C5-C20 aryl or heteroaryl group wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, -CN, and

x represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

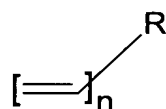
The vinyl-containing phosphonic acid can additionally contain even more organic solvents and/or water. These may positively influence the processibility. In particular,

the swelling of the polymer can be improved by addition of the organic solvent. The concentration of vinylphosphonic acid in such solutions is at least 5% by weight, preferably at least 10% by weight, particularly preferably between 10 and 97% by weight.

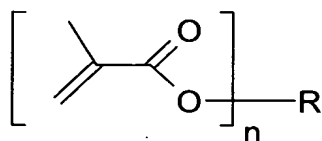
Commercially available vinylphosphonic acid, such as it is available from the company Aldrich or Clariant GmbH, for example, is particularly preferably used. The vinylphosphonic acid has a purity of more than 90%, preferably a purity of more than 97%.

In another embodiment of the invention, the vinyl-containing phosphonic acid contains further monomers capable to cross-linking. These are in particular compounds which have at least 2 carbon-carbon double bonds. Preference is given to dienes, trienes, tetraenes, dimethylacrylates, trimethylacrylates, tetramethylacrylates, diacrylates, triacrylates, tetraacrylates.

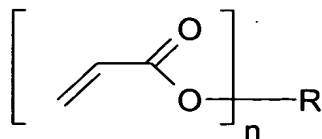
Particular preference is given to dienes, trienes, tetraenes of the formula



dimethylacrylates, trimethylacrylates, tetramethylacrylates of the formula



diacrylates, triacrylates, tetraacrylates of the formula



wherein

R represents a C1-C15 alkyl group, a C5-C20 aryl or heteroaryl group, NR',
-SO₂, PR', Si(R')₂, wherein the above-mentioned radicals themselves can be
substituted,

R' represents, independently of another, hydrogen, a C1-C15 alkyl group, a C1-
C15 alkoxy group, a C5-C20 aryl or heteroaryl group, and

n is at least 2.

The substituents of the above-mentioned radical R are preferably halogen, hydroxyl,
carboxy, carboxyl, carboxylester, nitriles, amines, silyl, siloxane radicals.

Particularly preferred cross-linking agents are allylmethacrylate, ethylene glycol
dimethylacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethylacrylate,
tetraethylene and polyethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate,
glycerol dimethacrylate, diurethane dimethacrylate, trimethylpropane trimethacrylate,
N',N'-methylene bisacrylamide, carbinol, butadiene, isoprene, chloroprene,
divinylbenzene and/or bisphenol A dimethylacrylate.

The crosslinkers are employed at between 0.5 to 30% by weight, based on the vinyl-
containing phosphonic acid.

Instead of a solution, it is also possible for the vinylphosphonic acid-containing
solution to also further contain suspended and/or dispersed components.

The swelling of the film in step A) takes place at temperatures above 0°C, preferably
between room temperature (20°C) and 160°C. In principle, the swelling can also take
place at lower temperatures, however, the period of time required for the swelling is
increased and thus the profitability reduced. The film used for the swelling can be

damaged at temperatures that are too high. The swelling time depends on the chosen temperature. The treatment time is to be chosen such that the desired swelling is achieved.

5 If the vinylphosphonic acid-containing solution used in step A) contains no starter solution, this is applied to the swelled film following step A). This can be performed by means of measures known per se (e.g., spraying, immersing) which are known from the prior art. If the polymerisation is otherwise initiated (e.g. thermally, photochemically, electrochemically), it is possible to dispense with a starter.

10 The starter solution contains at least one substance capable to form radicals. The formation of radicals can take place thermally, photochemically, chemically and/or electrochemically.

15 Suitable radical formers are azo compounds, peroxy compounds, persulphate compounds or azoamidines. Non-limiting examples are dibenzoyl peroxide, dicumene peroxide, cumene hydroperoxide, diisopropyl peroxydicarbonate, bis-(4-t-butylcyclohexyl) peroxydicarbonate, dipotassium persulphate, ammonium peroxydisulphate, 2,2'-azobis-(2-methylpropionitrile) (AIBN), benzopinacol, dibenzyl
20 derivatives, methylethylene ketone peroxide, as well as the radical formers available from the company DuPont under the name @Vazo and @Vazo WS.

Usually, between 0.0001 and 1% by weight (based on the vinyl-containing phosphonic acid) of radical former is added. The amount of radical former can be
25 varied according to the degree of polymerisation desired.

The polymerisation of the vinyl-containing phosphonic acid takes place at temperatures above room temperature (20°C) and below 200°C, preferably at temperatures between 40°C and 150°C, in particular between 50°C and 120°C. The
30 polymerisation preferably takes place at normal pressure, but may also take place with action of pressure. The polymerisation leads to a further solidification of the flat structure. Depending on the desired degree of polymerisation, the flat structure is a self-supporting membrane. The degree of polymerisation is preferably at least 30

repeating units, in particular at least 50 repeating units, particularly preferably at least 100 repeating units.

5 The polymerisation can also take place by action of IR or NIR (IR = infrared, i.e. light having a wavelength of more than 700 nm; NIR = near-IR, i.e. light having a wavelength in the range of about 700 to 2000 nm and an energy in the range of about 0.6 to 1.75 eV), respectively. Another method is exposure to β rays, γ rays and/or electron rays. In this connection, the irradiation dose is from 5 and 200 kGy.

10 The intrinsic conductivity of the membrane according to the invention is at least 0.001 S/cm, preferably at least 10 mS/cm, in particular at least 20 mS/cm.

15 The polymer membrane according to the invention contains between 0.5 and 97% by weight of the polymer as well as between 99.5 and 3% by weight of polyvinylphosphonic acid. The polymer membrane according to the invention preferably contains between 3 and 95% by weight of the polymer as well as between 97 and 5% by weight of polyvinylphosphonic acid, particularly preferably between 5 and 90% by weight of the polymer as well as between 95 and 10% by weight of polyvinylphosphonic acid. The polymer membrane according to the invention can
20 additionally contain even more fillers and/or auxiliary materials.

The polymer membrane according to the invention has improved material properties compared to the doped polymer membranes previously known. In particular, they already exhibit an intrinsic conductivity in comparison to known undoped polymer
25 membranes. The reason for this is in particular a polymeric polyvinylphosphonic acid present.

Possible fields of use for the polymer membranes according to the invention include, amongst others, the use in fuel cells, electrolysis, capacitors and battery systems.
30 Owing to their property profile, the polymer membranes are preferably used in fuel cells.

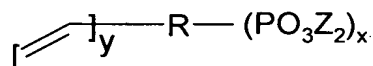
The present invention also relates to a membrane electrode unit which includes at least one polymer membrane according to the invention. For further information on

membrane electrode units, reference is made to the technical literature, in particular the patents US-A-4,191,618, US-A-4,212,714 and US-A-4,333,805. The disclosure contained in the above-mentioned citations [US-A-4,191,618, US-A-4,212,714 and US-A-4,333,805] with respect to the structure and production of membrane electrode assemblies as well as the electrodes, gas diffusion layers and catalysts to be chosen is also part of the description.

In another variant, the membrane according to the invention is applied to a catalytically active layer and this can be connected with a gas diffusion layer. In a variant, the catalyst can be applied together with the starter solution. These structures are also an object of the present invention.

A membrane electrode unit which contains at least one polymer membrane according to the invention, possibly in combination with another polymer membrane based on polyazoles and a polymer blend membrane is likewise an object of the present invention.

1. A proton-conducting electrolyte membrane which can be obtained by a method comprising the steps of
 - A. swelling a film made of at least one polymer in a vinylphosphonic acid-containing solution and
 - B. polymerising the present vinylphosphonic acid-containing solution introduced in step A).
2. The membrane according to claim 1, characterized in that the film used in step A) has a swelling of at least 3% in the vinylphosphonic acid-containing solution.
3. The membrane according to claim 1, characterized in that the polymers used in step A) are polymers stable at high temperatures which contain at least one nitrogen, oxygen and/or sulphur atom in one or different repeating units.
4. The membrane according to claim 1, characterized in that the solution of vinyl-containing phosphonic acid present in step A) is a compound of the formula



wherein

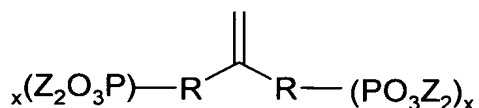
R is a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group, or a C5-C20 aryl or heteroaryl group, wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, COOZ, -CN, NZ₂,

Z represent, independently of another, hydrogen, a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group or a C5-C20 aryl or heteroaryl group wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, -CN, and

x represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10

y represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10

and/or of the formula



wherein

R is a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group, or a C5-C20 aryl or heteroaryl group, wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, COOZ, -CN, NZ₂,

Z represent, independently of another, hydrogen, a C1-C15 alkyl group, a C1-C15 alkoxy group, an ethyleneoxy group or a C5-C20 aryl or heteroaryl group wherein the above-mentioned radicals themselves can be substituted with halogen, -OH, -CN, and

x represents an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

5. The membrane according to claim 1, characterized in that the solutions of vinyl-containing phosphonic acid contain further monomers capable to cross-linking.

6. The membrane according to claim 1, characterized in that the solutions of the vinyl-containing phosphonic acids in step A) contains at least one substance capable to form radicals.

7. The membrane according to claim 1, characterized in that the substance capable to form radicals is applied as a solution following step A), but before step B).

8. The membrane according to claim 1, characterized in that it has an intrinsic conductivity of at least 0.001 S/cm.

9. The membrane according to claim 1, characterized in that it contains between 0.5 and 97% by weight of the polymer and between 99.5 and 3% by weight of polyvinylphosphonic acid.

10. The membrane according to claim 1, characterized in that it has a layer containing a catalytically active component.

11. A membrane electrode unit containing at least one electrode and at least one membrane according to one or more of claims 1 to 10.

5 12. A fuel cell containing one or more membrane electrode units according to claim 11 and/or one or more membranes according to any one of claims 1 to 10.

Abstract

2002/CVG 003

Method for producing a polymer electrolyte membrane and application thereof in fuel cells

5

The present invention relates to a proton-conducting polymer electrolyte membrane based on polyvinylphosphonic acid polymers which can, owing to its excellent chemical and thermal properties, be used for a variety of purposes and is particularly suitable as a polymer electrolyte membrane (PEM) in so-called PEM fuel cells.

10